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(54) METHOD OF APPLYING A PLASTICS TO A VULCANIZED RUBBER

(71) We, DUNLOP LIMITED, a British Company of Dunlop House, Ryder Street, St. James's, London S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

This invention relates to the application of thermoplastic plastics to vulcanized rubbers and is an improvement in or modification of U.K. Patent Serial No. 1,456,855.

According to the present invention, a method of applying a film of a thermoplastic plastics to the surface of a vulcanized rubber comprises causing relative frictional movement between the plastics and the rubber to melt the contact surface of the plastics, and moving the plastics and/or the rubber in relation to each other, whilst continuing said relative frictional movement, to leave a trail of the plastics on the rubber.

By this method, films of high or low strength plastics may be applied, e.g. as decoration, labelling, a potential hot-melt adhesive, or to confer desired properties on the rubber surface e.g. compatability with other materials or improvement of its ozone resistance.

The thermoplastic plastics may be in the form of a rod held in the chuck of a rotating or oscillating drill. When the surface of the rod in contact with the rubber has melted the rod is moved across the surface of the rubber so that a trail of the plastics is deposited. The rubber may be textile reinforced e.g. with nylon and if the surface to be moved relatively in contact with a plastics is uneven, it may be prebuffed.

The relative frictional movement between the plastics and the rubber may be produced in any convenient manner. One or both components may be moved. The friction may be achieved by rotary, angular or linear movement. The movement may be continuous, i.e. in one direction, or oscillatory. An alternative to mechanical movement is the use of an ultrasonic frequency welding technique which creates rapid small vibratory movement between the surfaces.

The conditions of the relative frictional movement, such as speed and duration of the movement and pressure between the plastics and the rubber, are such as to melt the friction surface of the plastics. A typical rate of frictional movement across a rubber is between 2.6×10^{-3} m/sec and 20.3×10^{-3} m/sec and a pressure of usually only about 100 to 500 kN/m² for 1 to 10 seconds is required. Of course, the conditions of application will depend on the materials used. Examples of suitable continuous relative rotary movement speeds are from 750 to 3000 revolutions per minute. When an oscillatory movement is employed, this may be performed over a few degrees of arc or, in the case of linear movement, over about 0.1—6 mm, preferably 1—4 mm, and at a frequency of 50—200 Hz, especially 100 Hz. External heating is not usually necessary but may be employed if desired.

Usually it is only necessary to raise the temperature of the plastics a few degrees above its melting point at its contact surface and therefore it can be cooled very rapidly and degradation of it or the substrate is unlikely.

The plastics and/or the rubber may be frozen to harden it for the relative frictional movement.

Separate films may be applied simultaneously by suitable equipment. Shaped films may be applied e.g. as a shoe outline by using e.g. linear or angular friction techniques.

Examples of compatible thermoplastic

plastics film materials and vulcanized rubber substrates are:

poly(vinyl chloride) with styrene/butadiene rubber; poly(ethylene terephthalate), poly-(tetramethylene terephthalate), polar elastoplastic linear block copolymers containing polyester blocks and polyether blocks, or polyformaldehyde, with polyepichlorhydrin or epichlorhydrin/ethylene oxide rubber; polyamides (preferably those with 3 to 12 methylene groups between the amide groups) with polyepichlorhydrin, sulphur-cured polyurethane, nitrile rubber or styrene/butadiene rubber; polycarbonates with nitrile rubber or polyepichlorhydrin; vinyl chloride polymers or styrene/acrylonitrile copolymers with nitrile rubber; methylmethacrylate resin with polyepichlorhydrin; substantially linear crystalline low pressure solution olefin polymers e.g. high density polyethylene, polypropylene or a copolymer of ethylene and/or propylene and/or a minor amount of butene-1, hexene-1 or a diene such as butadiene with ethylene/alphamonoolefin copolymer or ethylene/alphamonoolefin/diolefin terpolymer compositions containing up to 70% polymer; low density polyethylene or crystalline copolymers of ethylene with a vinyl alkanoic ester such as vinyl acetate, an alkyl acrylate such as ethyl acrylate or a vinyl halide such as vinyl chloride with ethylene/alpha-monoolefin copolymer or ethylene/alpha-monoolefin/diolefin terpolymer compositions containing up to 55% polymer; poly(ethylene terephthalate) or poly(tetramethylene terephthalate) with styrene/butadiene rubber, nitrile rubber or polybutadiene; polar elastoplastic linear block copolymers containing polyester blocks and polyether blocks with natural rubber, styrene/butadiene rubber, nitrile rubber, polyurethane rubber, acrylate rubber, polychloroprene, propylene oxide/unsaturated epoxide rubber or polybutadiene rubber; polyamides, preferably those with 3 to 12 methylene groups between the amide groups with vinylidene fluoride fluoroelastomers, natural rubber, polychloroprene, transpolypentenamer or polybutadiene rubber; polycarbonates with polybutadiene rubber; poly(vinylidene fluoride) with acrylate rubber; methyl methacrylate resin with nitrile rubber; poly(chlorotrifluoroethylene) with styrene/butadiene rubber; and polyurethane plastics with styrene/butadiene rubber or natural rubber. The polycarbonate may be a polyester of carbonic acid which is derived from dihydroxyl compounds in which the hydroxyl groups are directly attached to aromatic rings.

The rubber may be pre-treated i.e. treated before relative frictional movement with a plastics to enhance its adherability to the plastics film, for example the rubber may be pre-treated with a chemical treatment agent e.g. aldehyde condensation resin-forming ingredients such as resorcinol and hexamethylene tetramine, acidified sodium hyperchlorite, concentrated nitric acid, a chloro-isocyanuric acid such as trichloroisocyanuric acid suitably as a solution e.g. in ethyl acetate or as a powder, an alkali metal salt of a chloro-isocyanuric acid e.g. sodium dichloroisocyanurate, (such salts are commercially available under the trade name 'Fi-clor'), UV irradiation, glow discharge or flame-treatment. The term 'aldehyde condensation resin-forming ingredients' as used in this specification includes a partially condensed aldehyde resin. Alternatively and preferably a chemical treatment agent can be applied 'in situ' as the plastics film is applied to the rubber. This can be done either by forming or drilling at least one cavity in the plastics body and packing the cavities with a treatment agent or by forming into the required shape e.g. by moulding a blend of a plastics material and a treatment agent such as one of those already mentioned.

If desired the treatment agent may be supported in an inert medium e.g. a wax. When the plastics is in the form of a rod the cavity or cavities preferably extend longitudinally of the rod.

The plastics and/or the rubber may be in a compound with conventional ingredients such as plasticisers, tackifiers, softeners, fillers, pigments, antioxidants and stabilisers.

Incompatible substrates e.g. vulcanized nitrile rubber and vulcanized polychloroprene rubber may be bonded by applying a plastics film to each of them by the method of the present invention and then bonding the films e.g. by melting at least one of them and allowing the film or films to solidify in contact. Alternatively, a plastics interlayer may be placed between the film coated substrates and then the interlayer and usually also the films are melted and the assembly is allowed to cool.

The method of the present invention may be used in the manufacture of footwear. It is generally recognised that vulcanized rubber is the most durable material for footwear soles. The sole has to be attached to the upper of the article of footwear and previously this has uusually been done using an adhesive. If the adhesive is based on a conventional rubber solution e.g. one based on polychloroprene, this usually must be coated onto the sole and upper and allowed to dry to a slightly tacky state before the two components are pressed together. If a polyurethane-based adhesive is used, this must usually be coated onto both components and dried completely before bonding. The adhesive layer on the sole is then softened, e.g. using an infra red lamp, and the two components are pressed together. Both these methods are time-consuming because adhesive must be applied to sole and upper individually and the solvent in the adhesive allowed to evaporate before contacting the sole and upper. In addition it is usual to buff the adhering surfaces of the sole and upper before

applying an adhesive.

It is proposed to have a sole comprising a base of a vulcanized rubber composition having a layer or layers of a thermoplastic plastics bonded to it by the method of the present invention at places where the sole will eventually be attached to an upper. In order to attach the sole to an upper it is usually only necessary to soften at least the surface of the plastics, e.g. by infra red, ultrasonic, radio frequency or induction heating methods, and press the softened surface against the upper. Alternatively the surface of the plastics may be melted by using a friction welding tool. On cooling, a bond is obtained between the sole and the upper. No messy solvents are involved, and the process of bonding the upper to the sole is quicker and easier as it is not necessary to apply an adhesive to both sole and upper. Another advantage is that a sole can be easily transported already having a potential adhesive layer which can be bonded to an upper when required. It is also possible to use compositions for a sole based on rubbers which could not be used previously because they could not be bonded satisfactorily to an upper, e.g. a saturated ethylene/propylene copolymer rubber (commonly called EPM) or an unsaturated ethylene/propylene/diene terpolymer rubber (commonly called EPDM) e.g. an ethylene/propylene/ethylidene norbornene terpolymer rubber.

Examples of other applications of the method of the present invention are in the fabrication of rubber or rubberized containers, harnessing, furniture, belting and hose and in the retreading of tires.

The invention will now be illustrated in the following Examples:

EXAMPLE I.

Two sheets of rubber covered nylon fabric having a nitrile rubber composition on one side and a Neoprene composition on the other side manufactured by Dunlop Limited for flexible fuel tanks were positioned such that in one case the nitrile rubber compound (5635) and in the other the neoprene compound (5632) was facing upwards. A corresponding strip of at least 38 mm width on each sheet was buffed with a normal hand held sanding disc.

Against each buffed strip a rod measuring approximately 19 mm diameter by 30 mm long of a polar elastoplastic linear block copolymer containing polyester and polyester ether blocks and available as Hytrel 4055 from Du Pont was spun at 3000 rpm under a load of approximately 45 newtons down each edge such that at least 25.4 mm width was covered with a thin layer of Hytrel 4055. This was done by pulling each sheet under the molten end of the spinning plastics rod at a speed of 1 metre/minute.

One strip of fabric 50.8 mm wide was cut from each sheet at right angles to the frictioned edge. A sheet of Hytrel 4055 measuring 25.4 mm $\times$ 50.8 mm $\times$ 0.125 mm was placed between the two frictioned ends of the strips arranged to overlap a distance of 25.4 mm. The strips were positioned such that on testing the bond would be loaded in shear.

The overlap was placed in a press at 190°C with sufficient pressure to hold the two ends together. After 60 seconds the press was cooled until the Hytrel had solidified. The bonded strips were tested on a 10 ton Avery Universal Test Machine and failed at a force of 3380 newtons. Failure occurred in the fabric.

EXAMPLE II.

Example I was repeated except that the two neoprene surfaces were bonded together. The test piece failed at 2580 newtons with failure in the fabric.

EXAMPLE III.

The top edge of a standard styrene/butadiene rubber based wellington boot was frictioned as described in Example I, but against a rigid polyvinyl chloride (PVC) rod instead of Hytrel and the rubber surface had been pre-treated by painting with a 3% weight/volume solution of Fi-clor 91 (Trichloroisocyanuric acid) in ethyl acetate. A sheet of nylon reinforced polyvinyl chloride was then welded to the PVC coated rubber by means of a $3\frac{1}{2}$ KW Radyne Radio Frequency welder. The current was maintained until the PVC was seen to melt. On cooling the nylon reinforced polyvinyl chloride sheet was firmly attached to the rubber boot material with sufficient bond strength as to cause rubber failure when the bond was tested.

"FI-CLOR", "HYTREL", "AVERY" and "RADYNE" are Registered Trade Marks.

WHAT WE CLAIM IS:—

1. A method of applying a film of a thermoplastic plastics to the surface of a vulcanized rubber which comprises causing relative frictional movement between the plastics and the rubber to melt the contact surface of the plastics, and moving the plastics and/or the rubber in relation to each other, whilst continuing said relative frictional movement, to leave a trail of the plastics on the rubber.

2. A method according to claim 1 wherein the plastics and rubber are selected from the following groups viz. poly(vinyl chloride) with styrene/butadiene rubber, poly(ethylene terephthalate) or poly(tetra-methylene terephthalate) with nitrile rubber; poly(ethylene terephthalate), poly(tetramethylene terephthalate), polar elastoplastic linear block copolymers containing polyester blocks and polyether blocks, or polyformaldehyde with polyepichlorohydrin or epichlorohydrin/ethylene oxide rubber; polyamides with polyepichlorohydrin, sulphur-cured polyurethane, nitrile rubber or styrene/butadiene rubber; poly-

carbonates with nitrile rubber or polyepichlorohydrin; vinyl chloride polymers or styrene/acrylonitrile copolymers with nitrile rubber; methylmethacrylate resin with polyepichlorohydrin; substantially linear crystalline low pressure solution polymerised olefin polymers with ethylene/alpha-monoolefin copolymer or ethylene/alpha-monoolefin/diolefin terpolymer compositions containing up to 70% polymer; low density polyethylene or crystalline copolymers of ethylene with a vinyl alkanoic ester, an alkyl acrylate or a vinyl halide with ethylene/alpha-monolefin copolymer or ethylene/alpha-monolefin/diolefin terpolymer compositions containing up to 55% polymer; poly(ethylene terephthalate) or poly(tetramethylene terephthalate) with styrene/butadiene rubber or polybutadiene; polar elastoplastic linear block copolymers containing polyester blocks and polyether blocks with trans-polypentenamer, natural rubber, styrene/butadiene rubber, nitrile rubber, polyurethane rubber, acrylate rubber, polychloroprene, propylene oxide/unsaturated epoxide rubber or polybutadiene rubber; polyamides with vinylidene fluoride fluoro-elastomers, natural rubber, polychloroprene, trans-polypentenamer or polybutadiene rubber; polycarbonates with polybutadiene rubber; poly(vinylidene fluoride) with acrylate rubber; methyl methacrylate resin with nitrile rubber, poly(chlorotrifluoroethylene) with styrene/butadiene rubber; and polyurethane plastics with styrene/butadiene rubber or natural rubber.

3. A method according to claim 2 wherein the substantially linear crystalline low pressure solution polymerised olefin polymer is high density polyethylene, polypropylene or copolymer of ethylene or propylene with each other or with a minor amount of butene-1, hexene-1 or a diene, the vinyl alkanoic ester is vinyl acetate, the alkyl acrylate is ethyl acrylate, the vinyl halide of the ethylene copolymer is vinyl chloride, the polyamide has from 3 to 12 methylene groups between the amide groups, the polycarbonate is a polyester of carbonic acid which is derived from dihydroxyl compounds in which the hydroxyl groups are directly attached to aromatic rings, and the vinyl chloride polymer is poly(vinyl chloride), poly(vinyl dichloride) or poly(vinylidene chloride).

4. A method according to claim 1, 2 or 3 wherein the relative frictional movement is rotary, angular or linear mechanical movement.

5. A method according to claim 1, 2 or 3 wherein the relative frictional movement is produced by an ultrasonic frequency welding technique.

6. A method according to any of claims 1 to 5 wherein the surface of the rubber to be bonded is pretreated with UV irradiation, glow discharge or flame treatment.

7. A method according to any preceding claim wherein the plastics and rubber are moved in relation to each other for from 1 to 10 seconds and the pressure between them during the relative movement is from 100 to 500 kN/m².

8. A method according to any preceding claim wherein the relative frictional movement is continuous rotary movement at from 750 to 3000 revolutions per minute.

9. A method according to any of claims 1 to 7 wherein the relative frictional movement is oscillatory linear movement at a frequency of from 50 to 200 Hz.

10. A method according to any preceding claim wherein the vulcanized rubber is in the form of a footwear sole.

11. A method according to any preceding claim wherein the surface of the rubber to be bonded is pretreated with a chemical treatment agent.

12. A method according to claim 11 wherein the treatment agent is selected from concentrated nitric acid, acidified sodium hypochlorite, trichloroisocyanuric acid and sodium dichloroisocyanurate.

13. A method according to claim 11 wherein the treatment agent is selected from aldehyde condensation resin-forming ingredients, a hypochlorous acid generator, a chloroisocyanuric acid and an alkali metal salt of a chloroisocyanuric acid.

14. A method according to claim 13 wherein the treatment agent is resorcinol and hexamethylene tetramine.

15. A method according to any of claims 1 to 10 wherein the surface of the rubber is treated with a treatment agent as the plastics film is applied to it.

16. A method according to claim 15 wherein the treatment agent is in the form of a blend with the plastics.

17. A method according to claim 15 wherein the treatment agent is contained in at least one cavity in the plastics.

18. A method according to claim 17 wherein plastics is in the form of a rod and the or each cavity extends longitudinally of the plastics rod.

19. A method according to claim 17 or 18 wherein the treatment agent is supported in an inert medium.

20. A method according to claim 19 wherein the inert medium is a wax.

21. A method according to any of claims 15 to 20 wherein the treatment agent is selected from aldehyde condensation resin-forming ingredients, a hypochlorous acid generator, concentrated nitric acid, a chloroisocyanuric acid and an alkali metal salt of a chloro-isocyanuric acid.

22. A method according to claim 21 wherein the treatment agent is selected from resorcinol and hexamethylene tetramine, acidified sodium hypochlorite, trichloroisocyanuric acid and sodium dichloroisocyanurate.

23. A method according to any preceding

claim wherein the plastics is poly(vinyl chloride) and the rubber is styrene/butadiene rubber.

24. A method according to any preceding claim wherein the plastics and/or rubber is frozen to harden it for the relative frictional movement.

15. A method according to any preceding claim wherein the rubber is textile reinforced.

26. A method according to claim 25 wherein the textile is nylon.

27. A method of producing a plastics-film-coated vulcanized rubber according to claim 1 substantially as described in any one of the Examples.

28. A method of producing a plastics-film-coated vulcanized rubber according to claim 1 substantially as described herein.

29. A plastics-film-coated vulcanized rubber when made by the method according to any of the preceding claims.

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